

**METHOD OF SYNTHESIS OF METAL COMPLEXES OF TRIDENTATE
AZOMETHANE FROM 2-AMINOBENZAMIDE**

Seema Singh,

Department of Chemistry, N.R.E.C. College, Khurja, Bulandshahar, U.P., India.

Alok Gupta,

Department of Chemistry, Bundelkhand University, Jhansi, U.P., India.

Nizamul Haque Ansari,

Department of Chemistry, Rajdhani College, University of Delhi, New Delhi, India.

J. P. Singh,

Department of Chemistry, Bundelkhand University, Jhansi, U.P., India.

Shahla Khan,

Department of Applied Sciences, AFSET, Dhauj, Faridabad, Haryana, India.

Prakash Chandra,

Department of Chemistry, Bundelkhand University, Jhansi, U.P., India.

Raju Upadhaya,

Department of Applied Sciences, AFSET, Dhauj, Faridabad, Haryana, India.

ABSTRACT

The nobel series metal complexes of Mn (II), Ni(II) and Cu(II) were synthesized by two modes. In the first mode H₂-SAA binds to divalent metal ions viz., Mn (II), Ni(II) and Cu(II) ions through a ONO donor sequence in the enolized form. Enoxide bridging was reported for Ni(II) and Cu(II) complexes. The Ligands binds to trivalent metal ions in the non-enolized form through ONO donor set. Co(II) was observed to undergo oxidation to Co(III) during complexation. Cr (III) and Fe(III) complexes are reported to be phenoxide bridged dimeric compounds.

Keywords: Synthesis, Metal complexes, Tridentate Azomethane, 2-Aminobenzamide

Introduction

Transition metals and their derivative have inherent bio-potency, unique stereo and magnetic property ^[1]. The d-orbitals of a free transition metal atom or ion have same energy means they are (degenerate). However, when transition metals form coordination complexes, the d-orbitals of the metal interact with the electron cloud of the ligands in such a manner that the d-orbitals become non-degenerate (not all having the same energy). Transition metal complexes have contributed to the development in various fields of chemistry such as industrial, polymer, analytical, and bio-inorganic chemistry. This has attracted enormous interest in the synthesis of transition metal complexes with oxygen and nitrogen donor groups, due to the wide range of pharmacological activities of such compounds. Literature survey shows that studies on synthesis of coordination compound of transition metals are rare ^[2-5]. Keeping these in consideration, here in the present report we have investigated the method of synthesis of metal complexes derived from H₂-HNMAB using VO(II), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) ions.

Material and Methods

Synthesis of Metal Complexes

The following general procedure was adopted to synthesize the metal complexes ^[1]. To the methanolic solution of divalent/trivalent ^[2] metal chloride (0.001 mol) [Cr(III) 0.266 g; Mn(II) 0.198 g; Fe(III) 0.165 g; Co(II) 0.238 g; Ni(II) 0.237 g; Cu(II) 0.172g; Zn(II) 0.136g] hot methanolic suspension of H₂-HNMAB (2mmols, 0.580 g) was added in small increments. Ligand completely dissolves in metal ion to form clear solution. The pH of the solution was adjusted to 5-6 using methanolic ammonia. The mixture was refluxed for 3-4 h, filtered in hot condition and washed successively with methanol and ether and dried in vacuum. 0.163 g of vanadyl sulphate was used in case of oxovanadium (IV) complex and the same procedure was adopted. The purity of the complex was tested by TLC using different solvent mixtures. Yields: Oxovanadium (IV) 70%; Cr(III) 60%; Mn(II) 68%; Fe(III) 50%; Co(II) 65%; Ni(II) 50%; Cu(II) 75%, Zn(II) 50%.

Results and Discussion

Elemental Analysis

The complexes are soluble in 1, 4-dioxane, DMF and DMSO. They do not melt/decompose below 300 °C and stable under atmospheric conditions. The analysis of carbon, hydrogen, nitrogen, chlorine (wherever present) and metal (table 1) gives the following formulae [VO C₁₈H₁₄N₂O₃]₂; [CrC₁₈H₁₄N₂O₃Cl]₂; MnC₁₈H₁₈N₂O₅; [FeC₁₈H₁₄N₂O₃Cl]₂; CoC₁₈H₁₈N₂O₅; [NiC₁₈H₁₂N₂O₂]₂, [CuC₁₈H₁₂N₂O₂]₂; ZnC₁₈H₁₇N₂O₄Cl. Elemental analysis shows the metal to ligand ratio is 1:1 in all the complexes and presence of one chloride in Cr(III), Fe(III) and Zn(II).

Conductivity

The conductance measurements on solutions of complexes (Table-1) in 1×10⁻³ M DMSO reveal that all the complexes are non-electrolytes and the chloride present in Cr(III), Fe(III) and Zn(II) complexes is non-ionizable and occupy the inner (coordination) sphere.

Thermo gravimetric Analysis

Thermo gravimetric analysis of VO(II), Cr(III), Fe(III), Mn(II), Co(II) and Zn(II) complexes shows an weight loss of one mole of coordinated water per mole of the complex in case of VO(II), Fe(III) and Cr(III) complexes at 170 °C. In case of Mn(II), Co(II) complexes^[3], three moles of coordinated water is lost per mole of the complex. From the endotherms, it is established that the weight loss occurs at 165 °C and 180 °C for Mn(II) and Co(II) complexes respectively. In case of Zn(II) complex the weight loss occurs at 148 °C corresponding to two moles of coordinated water. It is further noted that the complexes decompose around 400 - 600 °C where they form metal oxides.

Infrared Spectra

The characteristic infrared spectral data of the ligands and metal complexes are presented in Table 2 and representative IR spectra of the complexes are given in Figure 1 to 3. The IR spectra of the metal complexes show that the ligand binds to metal ions in a tridentate manner. In all the complexes, except that of Zn(II) complex the ligand behaves as dibasic tridentate^[4]. The coordination to metal ions takes place through the deprotonated phenolic oxygen, deprotonated enolic oxygen and azomethine nitrogen and hence ONO donor. In case of Zn(II) complex, the

ligand is monobasic tridentate with ONO donor sequence, binding through the phenolic oxygen, azomethine nitrogen and carbonyl oxygen of amide moiety ^[5].

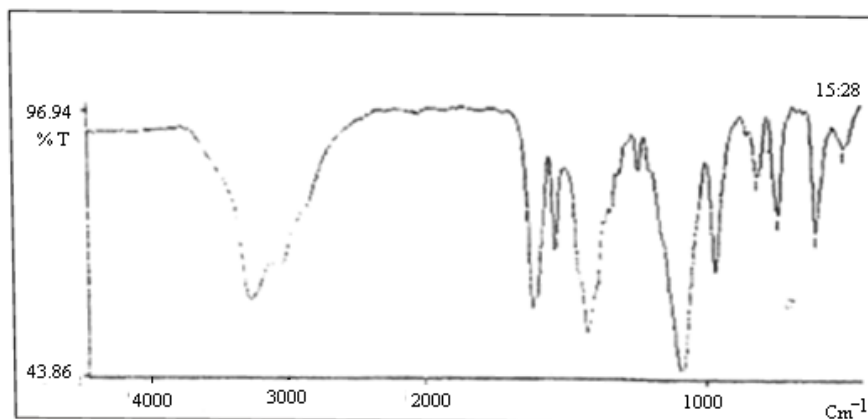


Figure: 1 IR spectrum of VO(II) H₂ – HNMA

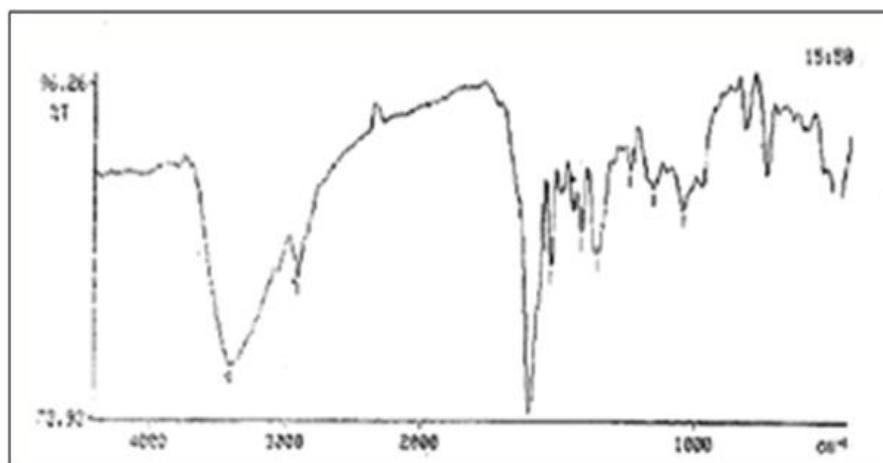


Figure: 2 IR spectrum of Fe(III) H₂ – HNMAB complex

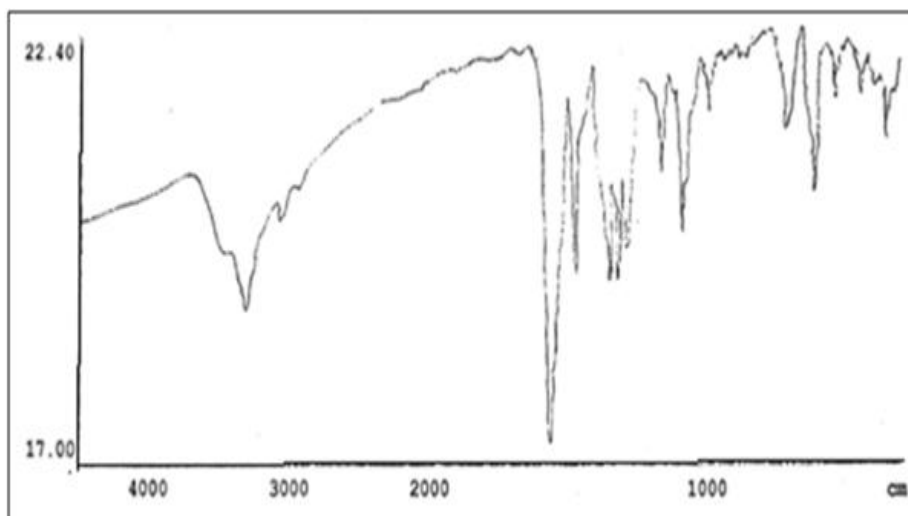


Figure: 3 IR spectrum of Cu(III) H₂-HNMAB Complex

The comparison of the infrared spectrum of the ligand with the spectra of metal complexes reveals specific changes in 3400-3050, 1670-1300 and 1000-280 cm⁻¹. The free ligand has sharp bands at 3385 and 3170 cm⁻¹ attributable to ν_{NH_2} and ν_{OH} undergo specific changes in the structures and intensities due to complex formation [6]. VO(II), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) complexes show a new strong band in the region at 3320-3200 cm⁻¹ assignable to $\nu_{\text{C=O}}$ and ν_{NH_2} of amide group at 1665 and 3385 cm⁻¹ which confirm enolization of amide group [7-8]. A new band formed in the region of 1619-1598 cm⁻¹ in these complexes, further supports enolization of amide group which is owing to formation of a new $\nu_{\text{C=N}}$ moiety during complexation [9]. The notable features of the complexes are the absence of bands assignable to ν_{OH} both phenolic [10] and enolic [11] suggesting participation of phenolic and enolic oxygens in metal binding process [12], which is further confirmed by the upward shift in $\nu_{\text{C-O}}$ (phenolic) [13], by 15-35 cm⁻¹. In Zn(II) complex the downward shift in $\nu_{\text{C=O}}$ by 11 cm⁻¹ and upward shift in ν_{NH_2} by 25 cm⁻¹ suggest that no enolization occurs during complexation and suggests binding to Zn(II) metal ion through the carbonyl oxygen [14]. However, the absence of ν_{OH} suggests that chelation occurs through the deprotonated phenolic oxygen. The positive shift in $\nu_{\text{C-O}}$ phenolic by 15 cm⁻¹ further supports this contention [15]. The free ligand has a strong and relatively sharp band at 1618 cm⁻¹ attributable to $\nu_{\text{C=N}}$ of azomethine group. In all the complexes

negative shift of this band to a range of 1537-1610 cm^{-1} indicates the involvement of azomethine nitrogen in chelation ^[16].

In VO(II), Cr(III) and Fe(III) complexes the high positive shift observed in $\nu_{\text{C-O}}$ (phenolic) by 27 to 35 cm^{-1} unambiguously establishes phenoxide bridging ^[17]. The position of $\nu_{\text{C-O}}$ (enolic) in Ni (II), Cu (II) complexes is relatively higher which may be attributed to possible enoxide bridging ^[18]. The free $\nu_{\text{C-O}}$ enolic is expected at 1300 cm^{-1} in case of Ni (II) and Cu (II) complexes. The positive shift due to $\nu_{\text{C-O}}$ phenolic is 15 cm^{-1} in these two complexes, compared to the shift of $\nu_{\text{C-O}}$ enolic which is 20 cm^{-1} . This observation suggests enoxide bridging, $\nu_{\text{C-O}}$ (enolic) is more significant than $\nu_{\text{C-O}}$ (phenolic). The positive shift in $\nu_{\text{C-O}}$ phenolic by more than +20 cm^{-1} has been reported as prerequisite for suggesting phenoxide bridging ^[19]. IR spectra of VO(II), Cr(II), Mn(II), Fe(III), Co(II), Zn(II) show broad troughs in the region of 3400-2985 cm^{-1} indicative of ν_{OH} of coordinated water as confirmed by thermal analysis. The coordinated nature of water is shown by the presence of bands at 950-978 and 645-570 cm^{-1} due to rocking and wagging modes respectively ^[20]. A strong non-ligand band in oxovanadium (IV) complex observed at 973 cm^{-1} is assigned to $\nu_{\text{V=O}}$ ^[21]. Further, the non-ligand bands observed in the range of 660-491 cm^{-1} are assigned to $\nu_{\text{M-N}}$ and $\nu_{\text{M-O}}$ modes ^[22] The $\nu_{\text{M-Cl}}$ band in Cr(III), Fe(III) and Zn(II) is identified at 330 and 278 cm^{-1} respectively. The peaks observed around 746 and 763 cm^{-1} are due to $\text{M}^{\text{O}}\text{M}$ in VO(II), Cr(III), Fe(III), Ni(II) and Cu(II) respectively ^[23].

It can be concluded that the ligand H₂-HNMA B acts; is a dibasic tridentate ONO donor in VO(II), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) complexes and monobasic tridentate ONO in case of Zn(II) complex. The coordination to metal ion takes place through the deprotonated phenolic oxygen deprotonated enolic oxygen, and azomethine monobasic tridentate with deprotonated phenolic oxygen, amide carbonyl-oxygen and azomethine nitrogen. It seems there is a transition of phenoxide bridging to enoxide bridging as the ionic radius increases ^[24].

Magnetic Moments

The magnetic moments calculated from room temperature susceptibilities and the electronic spectral data are presented in Table 3. The Oxovanadium (IV) complex show a magnetic moment value of 1.29 BM which is less than the expected value for a d¹ configuration.

This subnormal value may be ascribed to antiferromagnetism which can be due to interaction between electron spins on neighbouring metal ions. This sub normality of paramagnetic moment can be justified through phenoxide bridging ^[25]. Cr (III) complex has a magnetic moment value of 2.93 BM which is again indicating antiferromagnetic exchange operating between metal ions through phenoxide bridging. Mn(II) exhibits magnetic moment value of 5.95 BM which is in agreement with spin only value for high spin Mn(II) complex in d^5 configuration consistent with octahedral geometry ^[26]. Fe (III) has a magnetic moment value of 4.72 BM which is low for a d^5 system. Their low value can be attributed to weak metal-metal interaction and spin exchange through oxygen bridging ^[27]. Co (II) complex has a magnetic moment value of 4.26 BM which is expected for high spin octahedral complexes ^[28]. Ni (II) complex is diamagnetic giving a conclusive evidence for a square planar geometry ^[29]. In view of enolic oxygen bridging indicated by IR data dinuclear square planar geometry has been proposed. For Cu (II) complex the observed value is 1.69 BM which is consistent with d^9 configuration ^[30] with a possible square planar geometry.

Electronic Spectra

Comparative electronic spectral studies (table 3) of the ligand H₂-HNMAB and metal complexes show considerable modifications of the band structure, position and intensities from free ligand to metal complexes in 386-480 nm (25906-20833 cm^{-1}) region. This is due to involvement of amide and azomethine chromophores in metal binding process. Further, the complexes reveal characteristic d-d transitions assignable to various electronic transitions consistent with specific geometries. In the electronic spectrum of oxovanadium (IV) complex three bands have been identified at 13300, 16000 and 26666 cm^{-1} which are assignable to: ${}^2B_2 \rightarrow {}^2E$ (13300 cm^{-1}); ${}^2B_2 \rightarrow {}^2B_1$ (16000 cm^{-1}) and ${}^2B_2 \rightarrow {}^2A_1$ (26666 cm^{-1}) transitions respectively of a compressed octahedral geometry ^[31].

The three bands in the electronic spectrum of Cr(III) complex at 17851, 23980, 36363 cm^{-1} are in accordance with the three allowed : ${}^4A_2 \rightarrow {}^4T_2$; ${}^4A_2 \rightarrow {}^4T_1$ (F) and ${}^4A_2 \rightarrow {}^4T_1$ (P) transitions respectively of high spin six coordinate octahedral Cr (III) complexes ^[32]. The third band observed at 36363 cm^{-1} due to ${}^4A_2 \rightarrow {}^4T_1$ (P) transition may include some charge transfer contribution. Based on these observations dinuclear oxygen bridged octahedral geometry has

been proposed. Mn (II) and Fe (III) complexes have low intensity bands in the range of 9100-30600 cm^{-1} and high intensity band in the range of 33000 and 31250 cm^{-1} respectively. The low intensity bands are assigned to several doubly forbidden transitions ^[33] from 6A_1 to various high energy states like 4E_g , 4A_1 , 4E , 4G arising out of G, D, P, F terms. The high intensity bands could be due to spin and Laporte forbidden d-d transitions in admixture with charge transfer transitions. Monomeric octahedral geometry for Mn(II) complex and dimeric octahedral geometry for Fe(III) complex have been proposed. The electronic spectrum of Co (H) has a number of bands spreading over 9180, 16891, 23640 cm^{-1} . Based on the position and intensities these bands are assigned to the following transitions: ${}^4T_1 \rightarrow {}^4T_2$ (ν_1) (9180 cm^{-1}); ${}^4T_1 \rightarrow {}^4A_2$ (ν_2) (16891 cm^{-1}) and ${}^4T_1 \rightarrow {}^4T_1$ (P) (23640 cm^{-1}). The ratio of ν_2/ν_1 , is equal to 1.83 which supports octahedral geometry ^[34]. The electronic spectrum of Ni (II) reveals two distinct bands at 22600, 31150 cm^{-1} which are assigned to the transitions: ${}^4A_1 \rightarrow {}^1T_2$; ${}^1A_1 \rightarrow {}^1B_2$ respectively. These are in conformity with the square planar geometry ^[35] as supported by analytical, IR and magnetic susceptibility data. The electronic spectrum of Cu (II) shows a broad band with three components in the region of 13210-21739 cm^{-1} assignable to: ${}^2B_1 \rightarrow {}^2B_2$; ${}^2B_1 \rightarrow {}^2A_2$ and ${}^2B_1 \rightarrow {}^2E$ transitions corresponding to square planar geometry ^[36]. As the spectrum is recorded in DMSO solution, the possibility of solvent molecules occupying axial position in the square planar complex cannot be ruled out. As such the spectrum is probably representing the transformation of a real square planar complex into a distorted/elongated octahedral complex due to approach of solvent molecules.

¹H-NMR Spectrum of Zn(II) Complex

¹H-nmr spectrum of Zn(II) complex (Fig.4) was recorded in DMSO-d₆. The spectrum clearly indicates complexation of the ligand with Zn(II) ion as the azomethine proton shifts down field to δ 10.10 (s) compared to its position in the free ligand at δ 9.40. This observation confirms Zn(II) ion is bound through the azomethine nitrogen ^[37]. Further, the doublet observed in free ligand at δ 8.40 due to H-C₄ shows down field shift to δ 8.80 (d). The multiplet observed at δ 7.20-8.00 in free ligand shifts upfield to δ 6.60-8.00 with the merger of signal at δ 6.85 (d) (H-C₃) as a consequence of metal-ligand interaction resulting in extended conjugation in the chelated ring ^[38]. The signal identified at 53.30 is due to H₂O in DMSO-d₆. Zn(II) complex with

[ZnL(H₂O)₂Cl; L=Ligand] composition is proposed to have octahedral geometry based on analytical IR, ¹H- NMR data.

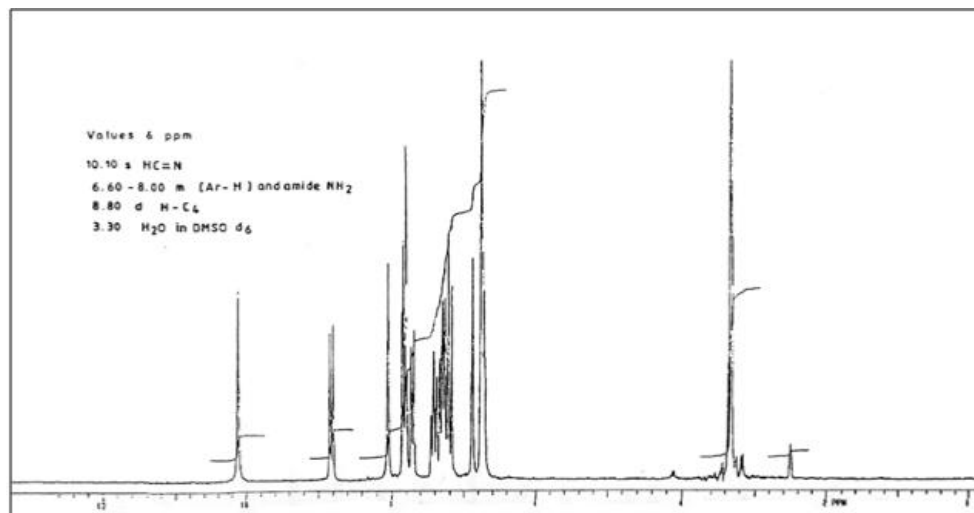


Figure: 4 ¹H – NMR Spectra of Zn(II) H₂-HNMAB

Table 1
Analytical Data of the Complexes of H₂-HNMAB

Found (Calcd) %			M ($\text{mhc}^2\text{mol}^{-1}$)	Complex (Molecular Formula)	Carbon	Hydrogen
Nitrogen	Chloride	Metal				
7.44 (7.50)	-	13.67 (13.65)	6.0	VO(II) ($\text{VOC}_{18}\text{H}_{14}\text{N}_2\text{O}_3$) ₂	57.96 (57.91)	3.77 (3.75)
7.15 (7.11)	8.99 (9.01)	13.00 (13.25)	17.0	Cr(III) ($\text{CrC}_{18}\text{H}_{14}\text{N}_2\text{O}_3$) ₂	54.81 (54.86)	3.51 (3.55)
7.08 (7.05)	-	13.82 (13.84)	7.0	Mn(II) ($\text{MnC}_{18}\text{H}_{14}\text{N}_2\text{O}_5$)	54.36 (54.41)	4.49 (4.53)
7.08 (7.04)	8.87 (8.93)	13.99 (14.05)	17.0	Fe(III) ($\text{FeC}_{18}\text{H}_{18}\text{N}_2\text{O}_5$)	54.52 (54.36)	3.53 (3.52)
6.94 (6.98)	-	14.66 (14.70)	5.0	Co(II) ($\text{CoC}_{18}\text{H}_{18}\text{N}_2\text{O}_5$)	53.91 (53.87)	4.52 (4.49)
8.10 (8.08)	-	16.95 (16.93)	5.0	Ni(II) ($\text{NiC}_{18}\text{H}_{14}\text{N}_2\text{O}_2$) ₂	62.32 (62.30)	3.41 (3.46)
7.99 (7.96)	-	18.10 (18.07)	6.0	Cu(II) ($\text{CuC}_{18}\text{H}_{14}\text{N}_2\text{O}_3$) ₂	61.47 (61.44)	3.39 (3.41)
6.58 (6.57)	8.37 (8.33)	15.30 (15.35)	18.0	Zn(II) ($\text{ZnC}_{18}\text{H}_{17}\text{N}_2\text{O}_4\text{Cl}$)	50.75 (50.72)	3.94 (3.99)

Table 2
Characteristic Infrared Frequencies of the Complexes of H₂-NHMAB (cm^{-1})

Compound	νNH_2 (amide)	$\nu\text{-OH}$ (phenolic)	$\nu(\text{N H})$ (new)	$\nu\text{C=O}$ (carbonyl)	$\nu(\text{C=N})$ (Azomethine) [$\nu(\text{C=N})$ (new enolic)]	$\nu\text{C-O}$ (phenolic)	$\nu\text{C-O}$ (enolic)	New Bands
Ligand	3385	3170	-	1665	1618	1350	-	
VO(II)	-	-	3246	-	1540	185	1320	973,746,6

Complex					[1619]			60-491
Cr(III) Complex	-	-	3320	-	1601 [1618]	1385	1320	982,763,6 60-491 330
Mn(II) Complex	-	-	3200	-	1698 [1619]	1356	1311	976, 660- 491
Fe(III) Complex	-	-	3223	-	1538 [1615]	1377	1305	950, 746, 660-491 278
Co(II) Complex	-	-	3207	-	1537 [1617]	1368	1311	978, 660- 491
Ni(II) Complex	-	-	3320	-	1537 [1619]	1365	1320	746, 660- 491
Cu(II) Complex	-	-	3293	-	1539 [1598]	1365	1320	763, 660- 491
Zn(II) Complex	3410	-	-	1654	1610	1365	-	972, 660- 491 278

Table 3
Magnetic Moments and Electronic Spectral Data of Complexes of H₂-HNMA B

Complex	μ(B.M.)	Electronic spectral bands ν_{\max} (cm⁻¹)
VO(II)	1.29	2666, 16000, 13300
Cr(III)	2.93	36363, 23980, 17851
Mn(II)	5.95	33000, 30600-9100
Fe(III)	4.72	31250, 30600-9100
Co(II)	4.26	23640, 16891, 9180
Ni(II)	Dia	31150,22600
Cu(II)	1.69	21739-13210

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